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DISTILLATION-AMALGAMATION METHODS FOR THE TECHNICAL DETERMINATION OF MERCURY IN ORES

BY

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DISTILLATION-AMALGAMATION METHODS FOR THE TECHNICAL DETERMINATION OF MERCURY IN ORES (1)

By C. W. Davis (2)

INTRODUCTION

The present active search for mining properties containing mercury and the interest being shown in the development and exploitation of domestic mercury mines call attention to the methods used for the control of these operations. A rough "practical" method that can be used in the field or at the mine is of primary importance to the prospector, miner, or plant operator. More accurate or "technical" methods of analysis are necessary to control the rough methods, to accurately follow the mining and metallurgical operations, and for the evaluation of such ores and other products as do not give satisfactory results by rough methods.

This paper touches on "practical" methods for mercury detection and estimation and refers to "wet" methods for the analysis of special mercury products but deals mainly with the "technical" methods characterized by distillation followed by amalgamation.

"PRACTICAL" METHODS FOR THE ESTIMATION OF MERCURY IN ORE

Cinnabar (HgS), the red sulphide, is the usual mercury mineral of commercial quicksilver ores. However, metallic mercury, occurring often as small scattered globules; calomel (Hg_2Cl_2), frequently gray, brown, or yellow in color; or a finely divided or amorphous sulphide which is red on fresh fractures but darkens on weathering may contribute to the mercury content.

(1) The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "This paper represents work done under a cooperative agreement between the U. S. Bureau of Mines and the University of Nevada. Reprinted from U. S. Bureau of Mines Information Circular 6202."

(2) Associate chemist, U. S. Bureau of Mines, Rare and Precious Metals Experiment Station, Reno, Nevada. Acknowledgment is made to the staff of the Mackay School of Mines and to the members of the Rare and Precious Metals Experiment Station for their valuable suggestions.

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Visual Inspection

The prospector familiar with mercury minerals is able to recognize high or medium grade mercury ore and can make a guess at the mercury content by a visual inspection; however, he may be misled by some unusual form such as the amorphous sulphide or the chloride which become darkened upon exposure. The actual content may be ascertained by breaking a lump of ore to expose a fresh surface, where the usual red sulphide or light-colored chloride may be observed if present.

A mining engineer experienced in the work is able to depend to a greater extent upon the use of visual observation, for he can make a fairly close estimate of the quantity of cinnabar, in place, in a mine by a visual study of the grade of ore observed at fixed intervals along cleaned faces, the specific gravity of all minerals being taken into consideration.(3)

Panning

A more accurate estimate of cinnabar content in an ore may be obtained by panning, or the brittleness of this mineral aids in its liberation from the gangue and its relatively high specific gravity (8 to 8.2) makes possible a clean gravity separation by washing. Some experienced panners have become very proficient in such work, so that this method is in wide use not only by the prospector but by the miner and plant operator as well.

The prospector relies on panning to tell him whether a property contains mercury and to aid him in guessing roughly at the amount present, but some experienced panners have become so proficient in the use of the pan that their accuracy in judging the mercury content of a cinnabar ore is well within the limit of error expected in sampling such material.

The proficiency that may be acquired is shown by the fact that a miner in Italy was always able to check assays within 0.1 per cent mercury(4) on high-grade ores, while he could make even better estimates on those of low grade.

Such refinement calls for constant practice based on adequate knowledge of the particular ore being used.

In a deposit consisting of a single type of ore the results of panning may be checked against the daily production if the amount of waste and the quantity of ore treated are known.

Accurate checking, however, demands assays and panning results on duplicate samples, for large errors would result from estimating the quantity of mercury in one sample by comparing the amount of its panned concentrate

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(3) Schuette, C. N., The Sampling and Estimation of Quicksilver Ore. Min. and Sci. Press, vol. 122, 1921, pp. 293-295.

(4) Oschatz, K., Die Verhüttung der Zinnobererze am Monte Amiata. Glückauf, 1918, Jahrg. 54, (2), p. 609.

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with that from a known, assayed product if in the two samples either the gangue or mercury minerals differed materially in specific gravity. Such an error might easily be made where crystalline cinnabar is the mercury mineral in one sample and amorphous mercury sulphide, such as frequently occurs in opal, contains the mercury in the other sample. The former red mineral is very heavy and has a high mercury content per unit volume, whereas the latter red mineral has a physical form which makes the mercury content per apparent unit volume much lower.

ASSAY METHODS

Assay methods are not only necessary for training and checking pan operators but are also essential for the determination of mercury in ores and other products where panning results are not accurate enough for the required purpose.

"Wet" Methods

Numerous wet methods (those involving dissolution of the mercury by some reagent) have been described in analytical text books and in chemical journals, and although these cover the accurate determination of mercury in all kinds of material, the methods are either too involved or require equipment or reagents that discourage adoption by technical assayers, especially by those who make only occasional mercury analyses.

Distillation-amalgamation methods are common practice in commercial laboratories and usually prove satisfactory if certain precautions and modifications are used, as will be explained later; on certain kinds of material, however, the results obtained by such a process are untrustworthy. Those assayers who have occasion to analyze a large number of ore samples or to test all sorts of mercury products, especially those which may give trouble by other methods, can not do better than to familiarize themselves with and use the methods and apparatus explained and described by Bouton and Duschak,(5) who state concerning its adaptibility: "The method can be applied to the determination of mercury in practically any material, including that containing considerable quantities of organic matter." With regard to speed they write: "With readily provided facilities one operator can make 50 to 60 determinations in an eight-hour day, and with an assistant at least 100 samples can be run, exclusive of the time required for crushing and grinding samples." With regard to accuracy these authors show that in products known to contain 0.0045 and 0.4806 gram of mercury, 0.0044 and 0.4799 gram were obtained by analysis using their method.

Distillation-Amalgamation Methods

Distillation-amalgamation methods because of their speed, simplicity, and the availability of the apparatus required are widely used for technical

(5) Bouton, C. M., and Duschak, L. H., The Determination of Mercury. Tech. Paper 227, Bureau of Mines, 1920, 44 pp.

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mercury assays in commercial laboratories. Although many varieties of the method, if carefully conducted, are capable of sufficient accuracy with most ores, a selection of the proper modification is necessary for correct results when certain mercury compounds or foreign substances are present.

The distillation-amalgamation methods in general consist of mixing the material to be analyzed (mercury ore) with some reagent or reagents that will liberate metallic mercury on heating; placing the mixture in a suitable container, the upper part of which is protected from the heat by a disk of some sort; covering the container with a snugly fitting sheet or foil of gold or silver, cooled by water or by contact with a cooled surface; heating the lower part of the container to volatilize the mercury, which collects on the cooled metal sheet; rinsing the deposit of mercury; drying and weighing the metal foil before and after the distillation. The increase in weight is considered to be due to mercury. The mercury on the metal sheet may be removed by heating, and the sheet may be used for another determination.

Procedure for Most Ores (Interfering Substances Absent)

Details of the foregoing method that have been found satisfactory for the routine assay of most mercury ores (those which contain no calomel or interfering foreign substances), using the Whitton apparatus, follow.(6) The same procedure with minor changes will be equally satisfactory for use in other distilling apparatus for sale by assay supply houses.

The ore sample, preferably from 0.15 to 2 grams or even 5 grams for a low-grade ore, should not contain over 0.1 gram of mercury. It is mixed thoroughly with about 6 grams of oil-free iron filings, placed in the retort, covered with about 3 grams of filings, and the charge then covered with about 2 grams of asbestos wool. (The latter covering prevents contents of the retort from contaminating the metal foil by the spattering of any condensed water that may drop back into the hot charge.) The weighed metal foil, either gold or silver, is clamped between the retort and its cover, the cover filled with water, and heat applied carefully to the bottom of the crucible. It is important that the temperature be not too high or a loss of mercury will result. To obtain the best conditions the apparatus may be placed over a Bunsen burner in such a way that the bottom of the retort is about 1¼ inches above the top of the burner, while the gas is so regulated that the blue inner cone just touches the retort and the flame runs up the sides of the retort about one-half inch. Such an arrangement will cause the water to boil in 6 or 7 minutes and to continue to boil, being replaced one or twice as evaporation proceeds. After heating about 20 minutes the apparatus is allowed to cool, and the foil is removed and then weighed. If the deposit is bright the increase in weight of the foil is due to mercury, but if a dark-colored deposit is obtained the result is probably unsatisfactory due either to faulty manipulation or to impurities in the ore which make some modification of the method necessary. The foil should always be ignited before use and should be kept clean and bright by scouring with some abrasive such as emery flour, when necessary.

(6) Whitton, W. W., The Determination of Mercury in Ores. Calif. Jour. Tech., vol. 4, 1904, pp. 33-39. Instructions from supply houses, accompanying Whitton apparatus.

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The form and material of the apparatus used in the distillation-amalgamation methods have been altered from time to time by various investigators.

According to the original Eschka method(7) the ore was mixed and covered with iron filings and placed in a porcelain crucible having a water-filled concave cover. The deposit resulting from distillation was dried in a desiccator over sulphuric acid. Teubner(8) made a modification in the container such that only a small portion of its gold cover was exposed to the mercury vapor, thus increasing the delicacy of the test. Chism(9) used a silver cover in place of gold and Holloway(10) endorsed its use. The latter cooled the silver cover by placing on it a metal vessel through which cold water was passed. Whitton(11) evolved an apparatus consisting of an iron crucible (passing through a metal disk) and an iron water cup between which a sheet of silver or gold was clamped. This is a very convenient device for routine mercury assays. James(12) recommends a nickel crucible with a silver water-cooled cover, which is also convenient. Either gold or silver covers for collecting the mercury are satisfactory, although gold covers may be used for a greater number of determinations than silver. A precaution in using the former is to use care in driving off the mercury because thin gold foil melts if held too long in the hottest part of a Meker flame.

The reagents used to liberate metallic mercury on heating have been the subject of considerable investigation, and it appears that the various difficulties encountered with certain mercury ores and products may be overcome by the proper selection and use of the reagents with which the ore is mixed if the usual precautions are taken to guard against mechanical loss, against contamination of the metal sheet on which the mercury is collected, and against loss through escape of mercury fumes.

Zdrahal(13) adapted the Eschka method to bituminous ores by washing the mercury deposit with alcohol or by destroying the organic matter by mixing minium with the ore and iron filings, and Hausamann(14) recommended lead chromate instead of minium as an oxidizer for ores high in bitumen.

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(7) Eschka, A., Beschreibung des Verfahrens zur Bestimmung des Quecksilbers in seinen Erzen. Oest. Ztschr. Berg.-Hut., Jahr. 20, 1872, pp. 67-68.
(8) Teubner, E., Qualitativ Probe auf Quecksilberspuren. Oest. Ztschr. Berg-Hut., Jahr. 27, 1879, p. 423.
(9) Chism, R. E., Abenderung der Eschka's Quecksilberprobe. Berg -Hut. ztg., Jahr. 58, 1899, pp. 149-50.
(10) Holloway, G. T., The assay of Mercury Ores. Eng. Min. Jour., vol. 83, 1907, p. 712; Analyst, vol. 31, 1906, pp. 68-71.
(11) Work cited.
(12) James, G. A., The James Apparatus for Quicksilver Determination. Eng. Min. Jour., vol. 90, 1910, pp. 800-801.
(13) Zdrahal, A., Die Eschka'sche Quecksilberprobe und ihre Genauigkeit. Oest. Ztschr. Berg-Hut., Jahr. 29, 1881, pp. 485-487.
(14) Hausamann, Oscar, Zur Eschka'sche Quecksilberprobe. Oest. Ztschr. Berg-Hut., Jahr. 29, 1981, p.561.

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Kroupa(15) modifies the reagents for ores of this type by using steel rolling-mill scale (Fe_3O_4) and zinc oxide in place of iron filings. The same modification was used by Janda(16). It is said to be applicable in the presence of sulphides of arsenic and antimony.

De Rubies(17) found that when ores containing calomel (Hg_2Cl_2) were assayed by the Eschka method there was a loss of mercury due to volatilization of the chloride. He overcame this difficulty by an adaptation of the distillation-amalgamation method, which is said to give accurate results, checked against electrolytic methods, even in the presence of compounds containing arsenic, antimony, tin, copper, silver, bismuth, cadmium, lead, vanadium, uranium, molybdenum, and sulphur.

Procedure for Dry Ores (Interfering Substances Present)

For dry ores the well powdered mercury ore (0.15 to 5 g. according to richness) was mixed with five times its weight of anhydrous, powdered potassium carbonate. The charge, placed in a crucible, was covered with a thin layer of potassium carbonate and finally by a layer of magnesium carbonate (or barium carbonate), both perfectly dry. (The upper layer acted as a filter for mercury vapor.) The metal foil and cooling device were placed on the crucible, and the operation of distillation was continued for 30 minutes. When the mercury deposit was not perfectly satisfactory, anhydrous powdered barium peroxide equal to the weight of the potassium carbonate was used in addition to the other constituents of the charge, and the assay was repeated the same as before except that toward the last of the distillation period the mixture was strongly heated to insure volatilization of all the mercury. (A higher temperature is required in the presence of BaO_2) The errors involved were of the order of 0.6 parts in 1000.

Procedure for Wet Ores (Interfering Substances Present)

For moist or wet ores that caused trouble by condensation of water on the metal foil so as to interfere with the deposition of mercury and cause spattering of the crucible contents when water dropped into the heated charge, de Rubies mixed the sample with several drops of a concentrated solution of sodium sulphide and dried at 105°C. Anhydrous powdered potassium carbonate equal to twice the weight of the sample was then mixed with about 6 grams of iron filings and with the sample; the charge was covered with potassium carbonate and magnesium carbonate as in the previous method, and the distillation proceeded as usual; 73.7 per cent mercury as against 73.88 per cent by the electrolytic method resulted in the presence of mixed salts of arsenic, antimony, tin, copper, silver, bismuth, cadmium, lead, vanadium, tungsten, and molybdenum.

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(15) Kroupa, G., Notigen zur Quecksilberstimmung nach A. Eschka. Berg-Hut. Ztg., Jahr. 49, 1890, p. 150.

(16) Janda, F., Die Ermittlung des Quecksilbers in Schwefelantimonund Schweferarsenhaltigen Quecksilber-fahlerzen mittels der Golddeckelprobe. Oest. Ztschr. Berg-Hut., Jahr. 47, 1899, pp. 205-208.

(17) de Rubies, S. P., Metodo muy exacto y rapido para valorar el mercurio en mayoria de sus compuestos. Anales Soc. espan. fis. quim., vol. 16, 1918, pp. 661-689.

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A development in the distillation-amalgamation method used in the laboratories of Letus S. Strickler of San Francisco, Calif., that is said to give reliable results in the presence of organic matter and to be unaffected by up to 150 milligrams of sulphur has recently been described.(18)

Metallic silver is used to combine with free sulphur, and a coating of copper oxide on the surface of iron filings is said to decompose hot organic gases. The silver is prepared by reducing silver chloride with aluminum or zinc, followed by washing, drying, and passing the product through a 40-mesh screen. The oxidized copper product is prepared by the addition, with thorough stirring, of 5 or 6 ounces of minus 40 plus 80 mesh iron filings to a solution containing 5 or 6 grams of copper sulphate, 2 or 3 c. c. of sulphuric acid and 150 c. c. of water. The product is washed, dried, and then roasted for several hours, with occasional stirring in an open iron pan over a naked flame. The hygroscopic material should be kept in a stoppered bottle when not in use.

Procedure by Strickler's Method

The following directions are given for conducting assays:

> For an average ore take the following: 5 or 6 grams of the copper oxide; about 2 grams calcium oxide; ore charge. Mix thoroughly and cover with copper oxide. For an ore containing much organic matter increase the cover.
>
> For an ore containing over 4 per cent elemental sulphur take the following: Copper oxide 5 or 6 grams; silver powder 2 to 3 grams; calcium oxide 2 to 3 grams; ore charge; mix thoroughly and cover with alternate layers of copper oxide and silver powder.
>
> Checks should be run with different quantities of ore, such as 1 gram against 2 grams, half a gram against 1 gram.

The Whitton apparatus is used in a somewhat modified form as explained below:

> Mr. Strickler finds it safer to keep the foil at a lower temperature than advised by Whitton. A piece of small brass tubing is soldered into the side of the cooling dish near the top for an overflow, and water is fed into the dish with a piece of rubber tubing from the hydrant. With this apparatus, some moisture in the charge is neces-

(18) Engineering and Mining Journal, "New Method for Quicksilver Analysis That is Simple and Reliable." vol. 126, 1928, p. 539.

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sary to insure the mercury amalgamating with the silver foil. With a dry ore, add two or three drops of water to the charge. Too much water will give low results. The mercury condenses on the drops of water on the foil and is lost, or, in case the foil is covered with a film of water, the mercury can not reach it. Only a sufficient amount to insure amalgamation should therefore be used.

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